

catena-Poly[[dinitratocopper(II)]- μ -4,4''-bis(1*H*-benzimidazol-1-yl)-1,1':4',1''-terphenyl]

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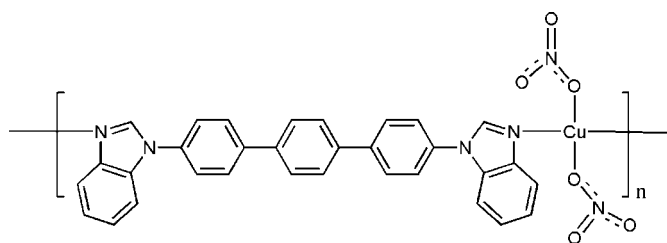
Received 10 April 2011; accepted 11 April 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.044; wR factor = 0.124; data-to-parameter ratio = 11.6.

In the title one-dimensional coordination polymer, $[\text{Cu}(\text{NO}_3)_2(\text{C}_{32}\text{H}_{22}\text{N}_4)]_n$, the Cu^{2+} ion (site symmetry 2) is coordinated by two nitrate O atoms and two N atoms from two 4,4''-bis(benzimidazol-1-yl)terphenyl (*L*) ligands in a distorted *cis*- CuN_2O_2 square-planar coordination geometry. An alternative description of the metal coordination geometry, if long Cu—O contacts to the bonded nitrate anions are considered, is an extremely distorted *cis*- CuN_2O_4 octahedron. The complete *L* ligand is generated by crystallographic twofold symmetry and connects the metal ions into infinite chains propagating in $[10\bar{1}]$. The dihedral angle between the benzimidazole ring system and the adjacent benzene (*B*) ring is $51.12(11)^\circ$ and the dihedral angle between the *B* ring and the central ring is $19.45(13)^\circ$.

Related literature

For background to benzimidazole-derived ligands in coordination polymers, see: Jin *et al.* (2006); Li *et al.* (2010); Su *et al.* (2003).



Experimental

Crystal data

$[\text{Cu}(\text{NO}_3)_2(\text{C}_{32}\text{H}_{22}\text{N}_4)]$	$V = 2685.7(9) \text{ \AA}^3$
$M_r = 650.10$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.960(3) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$b = 15.237(3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 12.139(2) \text{ \AA}$	$0.20 \times 0.18 \times 0.15 \text{ mm}$
$\beta = 103.94(3)^\circ$	

Data collection

Rigaku Mercury CCD diffractometer	13493 measured reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku/MS, 2005)	2371 independent reflections
$T_{\min} = 0.839$, $T_{\max} = 0.877$	2181 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	204 parameters
$wR(F^2) = 0.124$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
2371 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Cu1—N1	1.985 (2)	Cu1—O3	2.452 (3)
Cu1—O1	2.025 (2)		

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We thank the College Research Program of Yuncheng University [2008114] for funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5843).

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supplementary materials

Acta Cryst. (2011). E67, m603 [doi:10.1107/S1600536811013596]

***catena*-Poly[[dinitratocopper(II)]- μ -4,4''-bis(1*H*-benzimidazol-1-yl)-1,1':4',1''-terphenyl]**

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Comment

Benzimidazole has been well used in crystal engineering, and a large number of benzimidazole-containing flexible ligands have been extensively studied (Su *et al.*,2003; Jin *et al.*,2006). However, to our knowledge, the research on benzoimidazole ligands bearing rigid spacers is still less developed (Li *et al.*,2010).

Single-crystal X-ray diffraction analysis reveals that the title compound (I) crystallizes in the monoclinic space group $C2/c$. The geometry of the Cu(II) ion is surrounded by two benzoimidazole rings of individual **L** ligands and two nitrate anions, which illustrates a distorted square coordination environment (Fig. 1). Notably, as shown in Fig. 2, the four-coordinated Cu(II) center is bridged by the linear ligand **L** to form an infinite one-dimensional architecture.

Experimental

A mixture of CH₃OH and CHCl₃ (1:1, 8 ml), as a buffer layer, was carefully layered over a solution of 4,4'-Bis(benzoimidazol-1-yl)terphenyl (**L**, 0.06 mmol) in CHCl₃ (6 ml). Then, a solution of Cu(NO₃)₂ (0.02 mmol) in CH₃OH (6 ml) was layered over the buffer layer, and the resultant reaction was left to stand at room temperature. After *ca* three weeks, green block single crystals appeared at the boundary. Yield: ~30% (based on **L**).

Refinement

C-bound H atoms were positioned geometrically and refined in the riding-model approximation, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$.

Figures

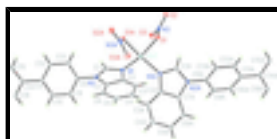


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

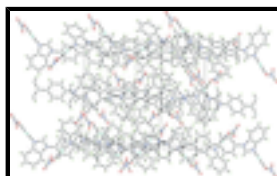


Fig. 2. The crystal packing for (I).

catena-Poly[[dinitratocopper(II)]- μ -4,4''-bis(1*H*-benzimidazol-1-yl)-1,1':4',1''-terphenyl]

Crystal data

[Cu(NO ₃) ₂ (C ₃₂ H ₂₂ N ₄)]	$F(000) = 1332$
$M_r = 650.10$	$D_x = 1.608 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -C 2yc	Cell parameters from 4661 reflections
$a = 14.960 (3) \text{ \AA}$	$\theta = 1.9\text{--}28.7^\circ$
$b = 15.237 (3) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$c = 12.139 (2) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 103.94 (3)^\circ$	Block, green
$V = 2685.7 (9) \text{ \AA}^3$	$0.20 \times 0.18 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Rigaku Mercury CCD diffractometer	2371 independent reflections
Radiation source: fine-focus sealed tube graphite	2181 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm^{-1}	$R_{\text{int}} = 0.044$
ω scans	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 1.9^\circ$
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku/MSC, 2005)	$h = -17 \rightarrow 17$
$T_{\text{min}} = 0.839$, $T_{\text{max}} = 0.877$	$k = -18 \rightarrow 18$
13493 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.124$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2 + 6.1716P]$
2371 reflections	where $P = (F_o^2 + 2F_c^2)/3$
204 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	1.0000	1.08431 (3)	0.7500	0.0158 (2)
N1	0.90976 (16)	1.00076 (15)	0.7873 (2)	0.0147 (5)
N2	0.79830 (16)	0.95918 (15)	0.8684 (2)	0.0127 (5)
N3	1.00584 (19)	1.19959 (17)	0.5927 (2)	0.0228 (6)
C1	0.86254 (19)	1.01906 (19)	0.8646 (2)	0.0149 (6)
H1A	0.8733	1.0684	0.9110	0.018*
C2	0.87224 (19)	0.92203 (18)	0.7368 (2)	0.0124 (6)
C3	0.89502 (19)	0.87094 (19)	0.6515 (2)	0.0144 (6)
H3A	0.9423	0.8872	0.6180	0.017*
C4	0.8443 (2)	0.79544 (19)	0.6192 (2)	0.0176 (6)
H4A	0.8587	0.7594	0.5641	0.021*
C5	0.7707 (2)	0.77168 (19)	0.6684 (3)	0.0177 (6)
H5A	0.7365	0.7217	0.6423	0.021*
C6	0.74853 (18)	0.82031 (18)	0.7533 (2)	0.0135 (6)
H6A	0.7009	0.8041	0.7862	0.016*
C7	0.80152 (19)	0.89544 (18)	0.7875 (2)	0.0119 (6)
C8	0.73918 (18)	0.96045 (18)	0.9471 (2)	0.0114 (6)
C9	0.7327 (2)	0.8866 (2)	1.0116 (3)	0.0189 (7)
H9A	0.7667	0.8365	1.0055	0.023*
C10	0.6748 (2)	0.88846 (19)	1.0852 (3)	0.0180 (6)
H10A	0.6696	0.8386	1.1273	0.022*
C11	0.62384 (18)	0.96369 (18)	1.0978 (2)	0.0113 (6)
C12	0.63268 (18)	1.03720 (18)	1.0321 (2)	0.0112 (6)
H12A	0.6000	1.0880	1.0391	0.013*
C13	0.68927 (19)	1.03586 (18)	0.9565 (2)	0.0116 (6)
H13A	0.6937	1.0850	0.9127	0.014*
C14	0.56072 (18)	0.96408 (18)	1.1761 (2)	0.0108 (6)
C15	0.52982 (19)	1.04264 (18)	1.2139 (2)	0.0129 (6)
H15A	0.5494	1.0958	1.1903	0.015*
C16	0.52938 (19)	0.88512 (19)	1.2128 (2)	0.0126 (6)
H16A	0.5478	0.8320	1.1875	0.015*
O1	1.06322 (14)	1.18409 (14)	0.68862 (19)	0.0224 (5)
O2	1.01639 (19)	1.26531 (16)	0.5384 (2)	0.0373 (6)
O3	0.94347 (17)	1.14482 (17)	0.5587 (2)	0.0352 (6)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0152 (3)	0.0149 (3)	0.0202 (3)	0.000	0.0099 (2)	0.000
N1	0.0161 (12)	0.0147 (12)	0.0160 (12)	-0.0024 (10)	0.0092 (10)	-0.0034 (10)
N2	0.0140 (12)	0.0135 (12)	0.0132 (12)	0.0014 (9)	0.0084 (10)	-0.0008 (9)
N3	0.0290 (15)	0.0182 (14)	0.0267 (15)	0.0031 (11)	0.0172 (13)	0.0032 (12)
C1	0.0163 (14)	0.0151 (14)	0.0151 (14)	-0.0004 (11)	0.0070 (12)	-0.0004 (12)
C2	0.0091 (13)	0.0161 (14)	0.0119 (14)	-0.0013 (10)	0.0024 (11)	0.0011 (11)
C3	0.0115 (13)	0.0217 (15)	0.0117 (14)	0.0037 (11)	0.0061 (11)	0.0003 (12)
C4	0.0203 (15)	0.0170 (15)	0.0152 (15)	0.0047 (12)	0.0037 (12)	-0.0035 (12)
C5	0.0196 (15)	0.0118 (14)	0.0202 (16)	-0.0010 (12)	0.0020 (12)	-0.0021 (12)
C6	0.0097 (13)	0.0134 (13)	0.0182 (15)	0.0005 (11)	0.0050 (12)	0.0044 (11)
C7	0.0130 (13)	0.0130 (13)	0.0108 (14)	0.0031 (11)	0.0053 (11)	0.0014 (11)
C8	0.0100 (13)	0.0145 (14)	0.0127 (14)	-0.0015 (11)	0.0085 (11)	-0.0011 (11)
C9	0.0200 (16)	0.0161 (15)	0.0262 (17)	0.0077 (12)	0.0164 (13)	0.0053 (13)
C10	0.0199 (15)	0.0145 (15)	0.0239 (16)	0.0048 (12)	0.0140 (13)	0.0085 (12)
C11	0.0103 (13)	0.0148 (14)	0.0097 (13)	-0.0005 (11)	0.0040 (11)	0.0004 (11)
C12	0.0112 (13)	0.0119 (14)	0.0113 (13)	0.0003 (10)	0.0044 (11)	-0.0013 (11)
C13	0.0140 (13)	0.0118 (13)	0.0100 (13)	-0.0020 (11)	0.0048 (11)	0.0015 (11)
C14	0.0096 (13)	0.0156 (14)	0.0086 (13)	0.0006 (10)	0.0046 (11)	0.0010 (11)
C15	0.0134 (13)	0.0118 (14)	0.0156 (14)	-0.0011 (11)	0.0078 (12)	0.0019 (11)
C16	0.0142 (13)	0.0130 (14)	0.0129 (14)	0.0015 (11)	0.0080 (12)	-0.0003 (11)
O1	0.0206 (11)	0.0194 (11)	0.0294 (12)	-0.0026 (9)	0.0102 (10)	-0.0009 (9)
O2	0.0480 (16)	0.0246 (13)	0.0474 (16)	0.0038 (11)	0.0273 (13)	0.0133 (12)
O3	0.0337 (14)	0.0330 (14)	0.0357 (14)	-0.0083 (11)	0.0020 (12)	0.0044 (11)

Geometric parameters (\AA , $^\circ$)

Cu1—N1	1.985 (2)	C5—C6	1.373 (4)
Cu1—N1 ⁱ	1.985 (2)	C5—H5A	0.9300
Cu1—O1 ⁱ	2.025 (2)	C6—C7	1.398 (4)
Cu1—O1	2.025 (2)	C6—H6A	0.9300
Cu1—O3	2.452 (3)	C8—C9	1.388 (4)
Cu1—O3 ⁱ	2.452 (3)	C8—C13	1.390 (4)
N1—C1	1.333 (4)	C9—C10	1.386 (4)
N1—C2	1.401 (4)	C9—H9A	0.9300
N2—C1	1.334 (4)	C10—C11	1.406 (4)
N2—C7	1.390 (4)	C10—H10A	0.9300
N2—C8	1.450 (3)	C11—C12	1.400 (4)
N3—O2	1.230 (3)	C11—C14	1.493 (4)
N3—O3	1.246 (4)	C12—C13	1.390 (4)
N3—O1	1.291 (4)	C12—H12A	0.9300
C1—H1A	0.9300	C13—H13A	0.9300
C2—C3	1.401 (4)	C14—C15	1.400 (4)
C2—C7	1.406 (4)	C14—C16	1.402 (4)
C3—C4	1.382 (4)	C15—C15 ⁱⁱ	1.394 (5)

C3—H3A	0.9300	C15—H15A	0.9300
C4—C5	1.420 (4)	C16—C16 ⁱⁱ	1.404 (5)
C4—H4A	0.9300	C16—H16A	0.9300
N1—Cu1—N1 ⁱ	100.24 (14)	C7—C6—H6A	121.9
N1—Cu1—O1 ⁱ	89.66 (9)	N2—C7—C6	131.9 (3)
N1 ⁱ —Cu1—O1 ⁱ	165.63 (9)	N2—C7—C2	105.4 (2)
N1—Cu1—O1	165.63 (9)	C6—C7—C2	122.6 (3)
N1 ⁱ —Cu1—O1	89.66 (9)	C9—C8—C13	120.8 (3)
O1 ⁱ —Cu1—O1	82.68 (12)	C9—C8—N2	119.8 (2)
C1—N1—C2	105.2 (2)	C13—C8—N2	119.4 (2)
C1—N1—Cu1	122.08 (19)	C10—C9—C8	119.1 (3)
C2—N1—Cu1	132.22 (19)	C10—C9—H9A	120.5
C1—N2—C7	107.8 (2)	C8—C9—H9A	120.5
C1—N2—C8	124.9 (2)	C9—C10—C11	121.8 (3)
C7—N2—C8	127.2 (2)	C9—C10—H10A	119.1
O2—N3—O3	123.4 (3)	C11—C10—H10A	119.1
O2—N3—O1	119.3 (3)	C12—C11—C10	117.5 (3)
O3—N3—O1	117.3 (2)	C12—C11—C14	121.4 (2)
N1—C1—N2	112.9 (3)	C10—C11—C14	121.0 (2)
N1—C1—H1A	123.5	C13—C12—C11	121.4 (3)
N2—C1—H1A	123.5	C13—C12—H12A	119.3
C3—C2—N1	131.0 (3)	C11—C12—H12A	119.3
C3—C2—C7	120.4 (3)	C8—C13—C12	119.4 (3)
N1—C2—C7	108.6 (2)	C8—C13—H13A	120.3
C4—C3—C2	117.2 (3)	C12—C13—H13A	120.3
C4—C3—H3A	121.4	C15—C14—C16	117.9 (3)
C2—C3—H3A	121.4	C15—C14—C11	121.4 (2)
C3—C4—C5	121.4 (3)	C16—C14—C11	120.7 (2)
C3—C4—H4A	119.3	C15 ⁱⁱ —C15—C14	121.21 (16)
C5—C4—H4A	119.3	C15 ⁱⁱ —C15—H15A	119.4
C6—C5—C4	122.0 (3)	C14—C15—H15A	119.4
C6—C5—H5A	119.0	C14—C16—C16 ⁱⁱ	120.89 (16)
C4—C5—H5A	119.0	C14—C16—H16A	119.6
C5—C6—C7	116.3 (3)	C16 ⁱⁱ —C16—H16A	119.6
C5—C6—H6A	121.9	N3—O1—Cu1	101.61 (16)
N1 ⁱ —Cu1—N1—C1	147.7 (3)	N1—C2—C7—C6	178.1 (2)
O1 ⁱ —Cu1—N1—C1	-21.8 (2)	C1—N2—C8—C9	-128.1 (3)
O1—Cu1—N1—C1	-79.4 (4)	C7—N2—C8—C9	49.3 (4)
N1 ⁱ —Cu1—N1—C2	-41.6 (2)	C1—N2—C8—C13	52.2 (4)
O1 ⁱ —Cu1—N1—C2	148.9 (3)	C7—N2—C8—C13	-130.4 (3)
O1—Cu1—N1—C2	91.3 (4)	C13—C8—C9—C10	0.6 (4)
C2—N1—C1—N2	0.1 (3)	N2—C8—C9—C10	-179.1 (3)
Cu1—N1—C1—N2	173.00 (18)	C8—C9—C10—C11	-1.2 (5)
C7—N2—C1—N1	-0.3 (3)	C9—C10—C11—C12	0.7 (4)
C8—N2—C1—N1	177.6 (2)	C9—C10—C11—C14	179.0 (3)
C1—N1—C2—C3	-179.0 (3)	C10—C11—C12—C13	0.4 (4)

supplementary materials

Cu1—N1—C2—C3	9.1 (5)	C14—C11—C12—C13	-178.0 (3)
C1—N1—C2—C7	0.1 (3)	C9—C8—C13—C12	0.4 (4)
Cu1—N1—C2—C7	-171.8 (2)	N2—C8—C13—C12	-179.9 (2)
N1—C2—C3—C4	-179.9 (3)	C11—C12—C13—C8	-0.9 (4)
C7—C2—C3—C4	1.0 (4)	C12—C11—C14—C15	-19.7 (4)
C2—C3—C4—C5	1.5 (4)	C10—C11—C14—C15	161.9 (3)
C3—C4—C5—C6	-2.7 (4)	C12—C11—C14—C16	159.3 (3)
C4—C5—C6—C7	1.0 (4)	C10—C11—C14—C16	-19.0 (4)
C1—N2—C7—C6	-177.8 (3)	C16—C14—C15—C15 ⁱⁱ	0.4 (5)
C8—N2—C7—C6	4.5 (5)	C11—C14—C15—C15 ⁱⁱ	179.4 (3)
C1—N2—C7—C2	0.3 (3)	C15—C14—C16—C16 ⁱⁱ	-1.5 (5)
C8—N2—C7—C2	-177.4 (3)	C11—C14—C16—C16 ⁱⁱ	179.5 (3)
C5—C6—C7—N2	179.4 (3)	O2—N3—O1—Cu1	170.1 (2)
C5—C6—C7—C2	1.6 (4)	O3—N3—O1—Cu1	-11.7 (3)
C3—C2—C7—N2	179.0 (3)	N1—Cu1—O1—N3	-28.9 (4)
N1—C2—C7—N2	-0.2 (3)	N1 ⁱ —Cu1—O1—N3	105.01 (17)
C3—C2—C7—C6	-2.7 (4)	O1 ⁱ —Cu1—O1—N3	-87.19 (17)

Symmetry codes: (i) $-x+2, y, -z+3/2$; (ii) $-x+1, y, -z+5/2$.

Fig. 1

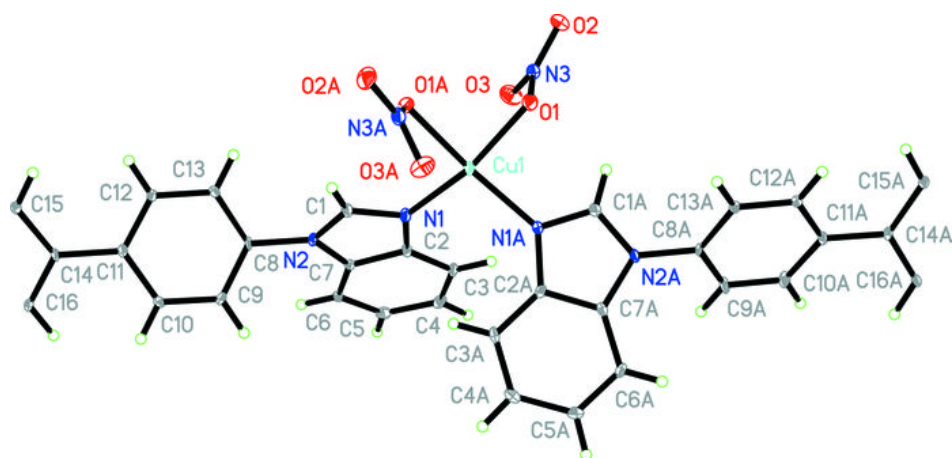


Fig. 2

